Nature Environment and Pollution Technology
An International Quarterly Scientific Journal
p-ISSN: 0972-6268 (Print copies up to 2016)
e-ISSN: 2395-3454
Vol. 23 | No. 3 | pp. 1723-1727 | 2024
Original Research Paper
https://doi.org/10.46488/NEPT.2024.v23i03.044
Open Access Journal

# Investigation of Rosemary Oil as Environmentally Friendly Corrosion Inhibitor of Aluminum Alloy

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**Nat. Env. & Poll. Tech.**
**Website: www.neptjournal.com**

*Received:* 18-05-2023
*Revised:* 03-07-2023
*Accepted:* 05-07-2023

**Key Words:**
Rosemary oil
Corrosion inhibitor
Aluminum alloy

## ABSTRACT

The inhibitory effect of Rosemary oil on the corrosion of aluminum alloy EN AW-2011 in 1M $H_2SO_4$ solution was studied by weight loss and electrochemical methods such as open circuit potential (OCP), linear sweep voltammetry (LSV) and linear polarization resistance (LPR). The inhibition efficiency increases with increasing the concentration and shows maximum inhibition efficiency (70.7 %) at optimum concentration (0.05 $g.L^{-1}$). The linear polarization resistance measurements show that the presence of Rosemary oil in 1M $H_2SO_4$ solution influences polarization resistance increasing and corrosion current decreasing. The voltammetric curve shows that Rosemary oil reduces the anodic process. Open circuit potential results confirmed that organic compounds present in Rosemary oil can form a protective layer on aluminum surfaces. The inhibitive effect was probably caused by the adsorption of organic compounds such as 1,8-cineole, α-pinene, borneol, limonene, and myrcene on aluminum surfaces which are non-toxic and environmentally friendly. This study showed that the essential oil of Rosemary could be used as an environmentally friendly inhibitor of the corrosion of alloy EN AW-2011 in an acidic medium.

## INTRODUCTION

Aluminum alloy EN AW 2011 is among the most preferred in machine building and the automotive industry due to the fact, that it is easy to process, has high mechanical strength, and allows coloring in various colors. There are various methods for protecting metals against corrosion, one of which is the addition of inorganic or organic corrosion inhibitors. In practice, organic corrosion inhibitors frequently are used in natural products – plant extracts from roots, leaves, and oils. Some plant extracts and essential oils can be used as organic ecological inhibitors. This is possible thanks to their molecules, containing heteroatoms such as O in polar groups or heterocyclic compounds with $\pi$-bonds (Khadraoui et al. 2013, Prabhu & Padmalatha 2013). The use of natural plant products to protect metals from corrosion is important because they show a high inhibitory efficiency of up to 98% and at the same time, they are environmentally friendly, non-toxic, and much more effective than the inorganic inhibitors (Sangeetha et al. 2013).

The plant extract and essential oil from *Mentha spicata* (Bensabah et al. 2013), *Terminalia ivorensis* extract (Wisdom et al. 2018), gum exudates from *Pachylobus edulis* in sodium chloride (Umoren et al. 2007), *Asparagus racemosus* extract (Bashir et al. 2019), *Ricinus communis* (Onukwuli et al. 2020), ethanolic extract of *Cordia dichotoma* seeds (Sharma & Sharma 2019) and *Glycine max* extract (El-Azaly 2019) in hydrochloric acid solution have a great importance in their use as environmental anti-corrosion products.

The literature review shows that the information about the essential oil of Rosemary (*Rosmarinus officinalis*) is limited but the investigation of the plant has great potential. The essential oil of Rosemary contains bicyclic monoterpene (α-pinene, -1,8cineol, borneol) and cyclic monoterpene (limonene) which are non-toxic and innocuous in the environment and biodegradable (Gonzalez-Minero et al. 2020).

Thanks to the adsorption of these organic compounds on the metal surface, a protective layer is formed, which reduces the corrosion.

This paper studies the inhibitory effect of Rosemary oil, used as an environmentally friendly inhibitor on the destruction of aluminum alloy EN AW-2011 in an acidic medium.

## MATERIALS AND METHODS

Aluminum alloy EN AW-2011 was used for all corrosion measurements. As an aggressive medium, 1M $H_2SO_4$, Pure

100% Rosmarinus officinalis essential oil was provided by “Rivana” (LLC, Bulgaria).

### Weight Loss Measurement

Before carrying out the weight loss experiments the samples were polished with abrasive papers with different grades (400-800), rinsed with acetone then with water, and dried. The samples were weighed and then placed in a test solution of 1M $H_2SO_4$ for 4 hours without the inhibitor and with Rosemary essential oil (0.01-0.05 $g.L^{-1}$) in the role of an inhibitor. 4 hours later, the samples were rinsed with distilled water, dried, and reweighed. The corrosion rate (W, $g.m^{-2}.h$) and the inhibition efficiency ($\eta_w$, %) of the alloy were determined by the equations:

$$W = \frac{\Delta m}{S.t} \quad \ldots(1)$$

$$\eta_w\,\% = \frac{W_{blank} - W_{inh}}{W_{blank}} \text{ x } 100 \quad \ldots(2)$$

where $\Delta m$ is the average weight loss of the sample (g); $S$ is the total area of the specimen ($m^2$); $t$ is immersion time (h), $W_{blank}$ is the corrosion rate values in the absence of inhibitor, and $W_{inh}$ in the presence of inhibitor.

### Electrochemical Measurements

The open circuit potential and linear sweep voltammetry were performed using the electrochemical workstation PalmSens and potentiostat/galvanostat (PAR model 263A) for linear polarization resistance. The obtained data were processed by the Power Suite program. All measurements were carried out in a three-electrode cell. A platinum wire as the auxiliary electrode, a Sat. Ag/AgCl electrode as a reference and aluminum alloy EN AW-2011 as a working electrode with an area of 1 $cm^2$.

The OCP was measured for 600 s. Linear sweep voltammetry measurement was performed at a scan rate of 0.010 V/s. The LPR measurements were performed from -0.020 V to +0.020 V vs. $E_{corr}$ at a scan rate of 0.10 mV $s^{-1}$.

Equation (3) was used to determine the inhibition efficiency ($\eta_p$ %) from linear polarization method data:

$$\eta_p\,\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \text{x} 100 \quad \ldots(3)$$

where $I_{corr}$ is the corrosion current value in the absence of an inhibitor and $I'_{corr}$ in the presence of an inhibitor.

### Surface Analysis

The surface of aluminum alloy specimens was examined by immersing them in various test solutions before and after exposure to 1M $H_2SO_4$ (blank) and with and without inhibitor of 0.05 $g.L^{-1}$ for 4 hours. A digital microscope (Digi Micro Scope 2,0M Pixels) was used to obtain the images of the specimen surface.

## RESULTS AND DISCUSSION

### Weight Loss Measurement

The values of percentage inhibition efficiency and corrosion rate obtained from weight loss measurement for aluminum alloy EN AW-2011 in 1M $H_2SO_4$ in the absence (blank) and presence of different concentrations of essential oil of Rosemary are summarized in Table 1. Inspection of the data in the table reveals that the addition of Rosemary oil decreases the corrosion rate of aluminum alloy EN AW 2011. This result indicates the inhibitive effect of the added essential oil of Rosemary on aluminum alloy corrosion in the acidic solution.

The inhibition efficiency increases as the concentration of added essential oil of Rosemary is increased. The optimal value of $\eta_w$ of 70.7% was received for 0.05 $g.L^{-1}$ of Rosemary oil.

### Electrochemical Measurements

**Open circuit potential:** The experiment with the OCP was conducted to investigate the effect of the Rosemary oil on the behavior of the aluminum alloy EN AW-2011 in 1M solution of $H_2SO_4$. Fig. 1 shows the current curves of the open circuit for the electrodes, made of Al 2011 and placed in 1M $H_2SO_4$ (a), and 0.01 $g.L^{-1}$ (b), 0.03 $g.L^{-1}$ (c), 0.05 $g.L^{-1}$ (d), placed in Rosemary oil.

During the first one or two minutes after the immersion into 1M $H_2SO_4$, the potential of the studied aluminum alloy quickly deviates in the negative direction and continues to deviate in the negative direction over time, i.e., the alloy breaks down in the 1M $H_2SO_4$.

After the addition of 0.01 $g.L^{-1}$ Rosemary oil to 1M $H_2SO_4$, the alloy potential initially deviates in the negative direction; but after the first minute it starts deviating in the positive direction and increases over the time of conducting the study. With the addition of 0.03 and 0.05 $g.L^{-1}$ Rosemary oil, the OCP value initially moves in the negative direction but then increases rapidly in the positive direction and

Table 1: Corrosion parameters of Al alloy EN AW 2011 in 1M $H_2SO_4$ and the presence of Rosemary oil (0.01-0.05 $g.L^{-1}$) determined by weight loss method.

| Concentration, $g.L^{-1}$ | W, $g/m^2.h$ | $\eta_w$, % | θ |
|---|---|---|---|
| blank | 0.0041 | - | - |
| 0.01 | 0.0018 | 56.1 | 0.561 |
| 0.03 | 0.0015 | 63.4 | 0.634 |
| 0.05 | 0.0012 | 70.7 | 0.707 |

remains approximately constant over time. It can be noted that with the increase in the oil concentration from 0.03 to 0.05 $g.L^{-1}$, the OCP value is shifted in the positive direction, i.e., the risk of corrosion decreases.

The deviation of the OCP in the negative direction at the beginning of the study period is probably due to the adsorption of the inhibitor molecules on the active side of the aluminum alloy (Radošević et al. 2001).

**Linear sweep voltammetry:** On the voltammetric curve, recorded for 1M $H_2SO_4$, a peak at a potential of 0 V (vs Ag/AgCl) (Fig. 2) is observed, which is associated with the oxidative reaction of intermetallic inclusions in the studied alloy, dissolving in an acidic medium (*Mrad* et al. 2017).

The presence of Rosemary oil reduces the anodic process, associated with the electrochemical oxidation of the aluminum alloy. The interaction between the organic substances in the Rosemary oil and the surface of the alloy affects the value of the potential and there is a slight shift in the positive direction. It is observed that the current value decreases almost in proportion to the concentration of the oil. Assuming that the current at this potential is associated with the destruction of the oxide layer, then it is evident that the presence of Rosemary oil decreases the current value almost proportionally with respect to the concentration of the oil. In addition, after the addition of Rosemary oil, a new peak appears at about 0.16 V (vs Ag/AgCl), which is associated with the oxidation of the monoterpene.

**Linear polarization resistance:** The linear polarization resistance experiment was conducted to establish the inhibitory effect of Rosemary oil on the corrosion of

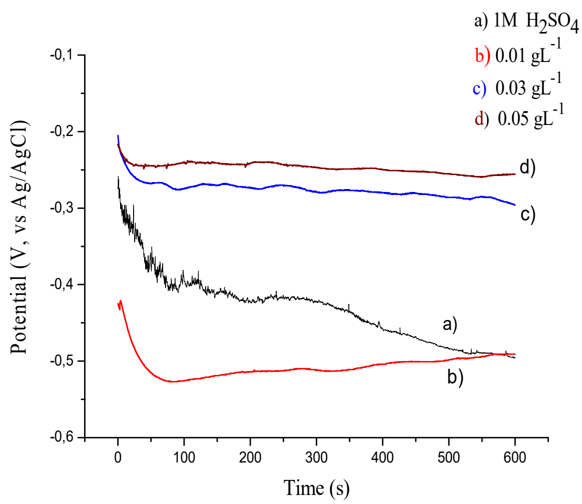


Fig. 1: OCP of Al alloy EN AW 2011 in 1M $H_2SO_4$ without and with Rosemary oil.

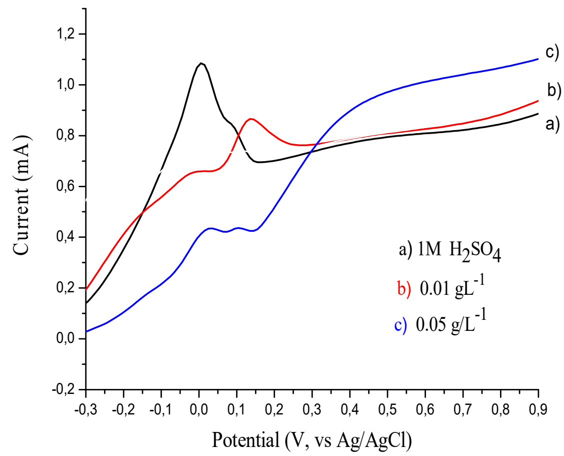


Fig. 2: Linear sweep voltammetry of aluminum alloy EN AW-2011 in 1 M $H_2SO_4$ without and with Rosemary oil.

Table 2: Electrochemical parameters of Al alloy EN AW 2011 in 1M $H_2SO_4$ and the presence of Rosemary oil (0.01-0.05 $g.L^{-1}$) determined by the LPR.

| concentration, $g.L^{-1}$ | $I_{corr}$ (μA) | CR (mpy) | Rp (kΩ $cm^{-2}$) | $\eta_p$, % |
|---|---|---|---|---|
| blank | 9.319 | 1.226 | 2.333 | - |
| 0.01 | 4.899 | 0.644 | 4.437 | 47.42 |
| 0.03 | 3.088 | 0.406 | 7.041 | 66.86 |
| 0.05 | 1.771 | 0.233 | 12.30 | 80.99 |

aluminum alloy 2011 in a 1 M $H_2SO_4$ and to determine the mechanism of inhibition. Table 2 presents the value of the corrosion current ($I_{corr}$), corrosion rate (CR), polarization resistance ($R_P$), and inhibition efficiency ($\eta_p$ %) for aluminum alloy 2011 in a 1 M solution of $H_2SO_4$ without and with Rosemary oil.

It can be observed that the values of Rp constantly increase with increasing Rosemary oil concentration, while the corrosion current and corrosion rate values decrease. The polarization resistance value is the highest at a concentration of 0.05 $g.L^{-1}$ Rosemary oil, while a higher Rp value indicates a lower corrosion rate.

According to data from Rivana, LLC, Bulgaria, the main components of Rosemary essential oil are 1,8-cineole, α-pinene, borneol, limonene, and myrcene.

Most of these components are monoterpene (bicyclic or cyclic monoterpene), having heteroatoms in their aromatic rings and they can be used as ecological corrosion inhibitors. These organic molecules can be adsorbed on the metal surface by the sharing electrons of an oxygen atom (such as a 1,8-cineole) or interactions between π-electrons of double bonds in the aromatic ring in monoterpene and vacant d-orbitals of aluminum (such as limonene) (Juergens et al. 2004, Bourazmi et al. 2018). As a result of these reactions is formed protective layer and thus reduces corrosion.

To understand the process of adsorption of the Rosemary oil on the surface of the aluminum alloy, the surface coverage values were fitted in the Langmuir adsorption isotherm and the values of the correlation coefficient ($R^2$) were used to determine the best fit.

A comparison of the obtained data from the weight loss and polarization method shows a good correlation between the two methods (Fig. 3). A correlation coefficient ($R^2$) from weight loss data is 0.998 and 0.995 from polarization data. In both methods a slope close to 1.

## Surface Analysis

The aluminum alloy coupons were immersed for 4 hours at room temperature in 1M $H_2SO_4$ with 0.05 $g.L^{-1}$ Rosemary oil in the role of an inhibitor. The surface morphologies of the aluminum alloy EN AW-2011 in 1M $H_2SO_4$ without and with the presence of an optimum concentration of inhibitor are recorded and shown in Fig. 4.

Many differences occur in both images. The aluminum alloy coupon, which was immersed in 1M $H_2SO_4$ without inhibitor (Fig. 4A), appeared to be heavily corroded when compared to the surface of aluminum alloy in the presence of Rosemary oil (Fig. 4B) due to the protective layer on the aluminum alloy surface. Microscopic pictures of the studied aluminum show that the presence of Rosemary oil in the solution changes the structure of the pores of the metal surface. Therefore, the corrosion rate decreases, since the adsorption of the inhibitor changes the mechanism of

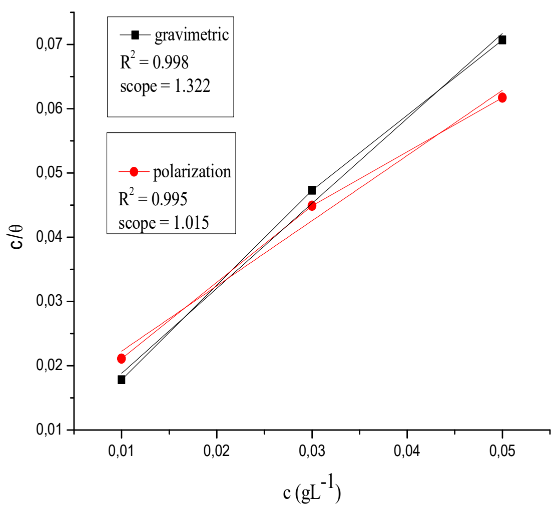


Fig. 3: Curve fitting of weight loss and polarization data obtained for aluminum alloy EN AW 2011 in 1M $H_2SO_4$ with Rosemary oil to Langmuir adsorption isotherm.

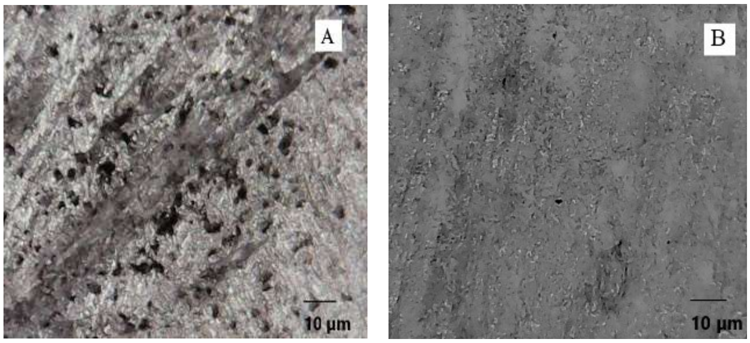


Fig. 4: Micrography of aluminum alloy EN AW-2011 surface A) in 1M $H_2SO_4$ and B) inhibited aluminum alloy (1M $H_2SO_4$ + 0.05 $g.L^{-1}$ Rosemary oil).

anodic dissolution and aluminum passivation during its stay in sulfuric acid.

## CONCLUSIONS

The essential oil of Rosemary (*Rosmarinus officinalis*) is organic in nature and can be used in the production of environmentally friendly inhibitors and it is one of the natural inhibitors which has an inhibitive action on the corrosion of metals. It contains various active organic compounds such as α-pinene, -1,8cineol, borneol, and limonene which are non-toxic and have no ecological hazards.

Weight loss measurements confirm that the Rosemary essential oil successfully inhibits the corrosion of aluminum alloy EN AW-2011 and the inhibition efficiency goes up with the increase in the concentration of the oil. Electrochemical measurements give reasons to conclude that the investigated Rosemary oil can be successfully used as a corrosion inhibitor for aluminum alloys in 1M $H_2SO_4$. The inhibition efficiency of the investigated essential oil depends on its concentration in the solution. This study proves that the essential oil of Rosemary (Rosmarinus officinalis) has a good ability to inhibit the corrosion of aluminum alloy EN AW 2011 in 1M $H_2SO_4$ and can used as an environmentally friendly inhibitor in this medium.

## ACKNOWLEDGEMENT

The author would like to thank the Research and Development Sector at the Technical University of Sofia for the financial support.

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